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13. ABSTRACT *(Maximum 200 words)*

Theories of the mechanical, vibrational, and electronic properties of III-V semiconductors have been developed and applied to (1) understanding the physics underlying the II-VI doping problem and suggesting band-gap engineering schemes for circumventing the problem; (2) making predictions of how the character of deep and shallow impuritkies can be different in superlattics from in bulk materials (3) understanding how surfaces of zincblende and wurtzite semiconductors relax, and how this relaxation depends on the ionicity of the semiconductor; (4) obtaining better insight into the properties of semiconducting alloys, both electronically and virbrationally, with attention paid to how ordering phenomena in these alloys affects their properties; (5) trying to determine if Si_x/Ge_{1-x} alloys or superlattices of these alloys can be made into reasonable efficient light-emitters; (6) predicting the effects of defects on the vibrational properties of semiconductors; and (7) producing simulations of semiconductor growth, including models of amorphous semiconductors, defect motions, anharmonic phonons near the melting point, studeis of melting mechanism, and reaction pathways.

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FINAL TECHNICAL REPORT
DATE: 20 March 1991
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TITLE: Vibrational, mechanical, and thermal properties of III-V semiconductors
PRINCIPAL INVESTIGATOR: John D. Dow

1. SUMMARY

Theories of the mechanical, vibrational, and electronic properties of III-V semiconductors have been developed and applied to (1) understanding the physics underlying the II-VI doping problem and suggesting band-gap engineering schemes for circumventing the problem; (2) making predictions of how the doping character of deep and shallow impurities can be different in superlattices from in bulk material; (3) understanding how surfaces of zincblende and wurtzite semiconductors relax, and how this relaxation depends on the ionicity of the semiconductor; (4) obtaining better insight into the properties of semiconducting alloys, both electronically and vibrationally, with attention paid to how ordering phenomena in these alloys affects their properties; (5) trying to determine if Si_xGe_{1-x} alloys or superlattices of these alloys can be made into reasonably efficient light-emitters; (6) predicting the effects of defects on the vibrational properties of semiconductors; and (7) producing simulations of semiconductor growth, including models of amorphous semiconductors, defect motions, anharmonic phonons near the melting point, studies of melting mechanisms, and reaction pathways.

2. OBJECTIVES

Our goal is to develop theories of the mechanical, vibrational, and thermal properties of III-V semiconductor alloys that will lead to a better understanding of the physics of these materials.

3. STATUS OF RESEARCH

We have made progress on the following problems:

A. Doping of II-VI semiconductors

For several decades attempts to dope large-gap semiconductors such as ZnSe p-type have been frustrated by the "self-compensation problem." As a result, efforts to develop efficient light-emitters in the blue and green have been frustrated. At first the "self-compensation problem" was believed to be a result of defect dynamics: a p-type dopant introduced into ZnSe would purportedly generate a vacancy that would compensate the dopant, rendering p-doping impossible. As a result, p-n junctions could not be fabricated in large-gap semiconductors, and so light-emitting diodes and lasers could not be fabricated in these materials. More recently people have reexamined the self-compensation problem, and many have concluded that the p-doping problem does not result from defect dynamics, but from dirty material. Our contribution has been to predict which impurities or "dirt" might inhibit p-doping and why. We have paid particular attention to a little-noticed fact: ZnTe is easily doped p-type (but difficult to dope n-type) while ZnSe is

almost impossible to dope p-type, but easily doped n-type. Hence study of the substitutional alloy $ZnSe_{1-x}Te_x$ should reveal vital clues to understanding the p-doping problem.

We have suggested that the origin of the problem is a naturally occurring defect that, in ZnTe, is an acceptor, but in ZnSe is a hole trap [239,241]. Our theory naturally produces such a native defect, the antisite defect Zn_{anion}. Thus this defect undergoes a shallow-deep transition as a function of alloy composition x in $ZnSe_{1-x}Te_x$. It is a deep hole trap in ZnSe and a powerful generator of holes in ZnTe, tending to make ZnSe semi-insulating and ZnTe p-type.

If this mechanism is correct -- and that remains to be seen -- then we can engineer the electronic structures of II-VI materials to make blue light emitters. Schemes we have thought of include straining the material in order to convert the deep hole trap in ZnSe into an acceptor, making superlattices of ZnSe with thin layers of small-gap materials such as GaAs (which would lead to green emission from the GaAs layers), and finding ways to grow the material so that the concentration of the offending defect is small.

B. Deep levels in superlattices

We have developed a theory of deep levels in superlattices, which shows how impurities can have different doping character in superlattices from in bulk material [225,228,253,254,261]. This theory predicts that shallow impurities can become deep traps and vice versa. This theory represents the first comprehensive treatment of deep levels and how they are affected by the structure of the superlattice.

C. Surface relaxation

We have discovered a new reconstruction of the zincblende (110) surface, a surface that was thought to have only the standard reconstruction described by the Rigid Rotation Model. This reconstruction is c(4×6), and appears to be metastable and cleavage-related.

We have also studied theoretically how semiconductor surfaces relax and how the amount of relaxation is related to their ionicity. Our results suggest that the Rigid Rotation Model, with a rotation angle of about 29^o for the anions to rigidly rotate out of the (110) surface is valid, but that the rotation angle depends on ionicity -- becoming smaller in the large-ionicity zincblende semiconductors. (This dependence on ionicity for large ionicity has been disputed by theorists using methods less-sophisticated than ours.) A similar result holds for wurtzite semiconductors [168,197,200,234,267].

D. Alloys

Our work on semiconducting alloys has had several facets.

We have examined $PbSn_{1-x}Te_x$ alloys and their electronic properties to determine if the fact that they undergo a Dimmock reversal causes them to exhibit significant deviation from virtual-crystal behavior. Such deviation does occur, but not for the bands relevant to electronic properties [180].

We have developed a new scheme for treating correlations in alloys, in which we use quantum Ising models to generate all levels of atomic correlations for an alloy, based on one measurement of low-order correlations, such as an EXAFS measurement of nearest-neighbor probabilities. The adjustable parameters of the Ising model (e.g., exchange coupling) are altered to reproduce the data on hand; the high-order correlations are generated using the Ising model; and then the electronic and vibrational properties of the alloy are computed. This scheme allows one to make reliable predictions of electronic and vibrational properties of correlated alloys, using as input only one piece of data about atomic correlations and the well-known properties of bulk semiconductors [207].

The electronic properties of partially ordered alloys have been worked out, using order-disorder models of semiconductors [224].

The large-gap semiconductor InN and its alloys $In_{1-x}Ga_xN$, $In_{1-x}Al_xN$, have been studied to determine if they can be doped in a way compatible with making light-emitters in the ultra-violet and blue. Emphasis here was on the doping properties to be expected, and whether p-n junctions could be fabricated [213].

E. Silicon-Germanium

Recently there has been a great deal of interest in alloys and superlattices of silicon and germanium. With this in mind, we have predicted the band structure of [111] superlattices involving Si_xGe_{1-x} with different compositions in its layers. Superlattices in the [111] direction have a better chance to be light emitters, because one folds the L rather than X minima of the conduction bands [218]. By suitably combining strain, period, and composition, it is possible to obtain a direct-gap superlattice. However, the light emission intensity is likely to be quite weak.

F. Phonons

We have developed an improved theory of phonons associated with defects in semiconductors, and have found unanticipated features of their normal modes -- which appear to explain long-standing anomalies [257].

We have also explained features of the phonon spectra of $Hg_{1-x}Cd_xTe$ alloys as associated with alloy correlations and fluctuations. The phonon spectra are much more sensitive to atomic correlations in alloys than the electronic structure, as a rule [181].

G. Molecular Dynamics

A major question that is difficult to answer theoretically is "Where are the atoms of a semiconductor?" At low temperatures for perfect semiconductors, the assumed answer to this question is the bulk crystal structure, and many of the methods of evaluating and predicting the electronic and vibrational properties of semiconductors assume this answer. At high temperatures, during chemical reactions, or when there are important atomic motions (such as during diffusion or impurity relaxation), it is often important to know the positions and trajectories of atoms -- and this is a difficult problem theoretically. Most often questions of atomic positions are best answered using Local Density

theory and minimizing the energy. This, however, is often a daunting task and requires a lot of computer time.

We have, in collaboration with Prof. Otto Sankey's group, embarked on a major project to make the computation of atomic trajectories feasible. We have developed a major computer program for a priori molecular dynamics of semiconductors, which is an order of magnitude faster computationally than the Car-Parrinello schemes. With this program we have predicted the anharmonic phonon spectra of crystalline Si and C, as well as the phonons of amorphous Si and C. This method predicts equilibrium and metastable structures of solids and clusters -- and promises to figure prominently in future work. With it, we expect to predict metastable semiconductor structures (for alloys in particular), diffusion pathways, and properties of semiconductors near the melting point [262]. Extension of this work to III-V semiconductors is in progress.

H. Scanning tunneling microscopy

We have developed a theory of scanning tunneling microscopy images and have used these images in collaboration with our experimental scanning tunneling microscopy program to explain the sizes of step-plateaux on the Si (110) surface, when strained [232].

I. Excitons in strained-layer superlattices

We have developed the first theory of core excitons in superlattices and strained-layer superlattices. We expect that this theory will eventually be useful for experimental studies of interface disorder, using synchrotron radiation spectroscopy [243].

J. Möbius transforms

We have helped develop the mathematics of Möbius transforms, an area that should be of interest to the Air Force, because it permits the reconstruction of the thermal distribution of a source from its black-body radiation spectrum [270]. In principle, one could construct the image of a radiating body from its spectrum.

K. Miscellaneous

We have in addition contributed to the theory of semiconductor crystallites [218] by showing how their spectral densities evolve with size, invented the concept of structure-modulated superlattices [233] and predicted their properties, studied the oxidation of GaAs [226], predicted the electronic structure of InP under high pressure [245], contributed to the Schottky barrier problem [251], and provided prescriptions for understanding how frontier orbitals in macromolecules or biomolecules might influence their abilities to undergo certain reactions [263].

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5. PROFESSIONAL PERSONNEL

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6. INTERACTIONS

The principal investigator has functioned as an advisor to the DuPont Corporation on a wide range of topics in materials science, electronics, and solid state physics, and to the Army (Dr. Ruth Nicolaides) on matters related to scanning tunneling microscopy.

PATENTS

None.